

# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3297

EFFECT OF OXYGEN CONTENT OF FURNACE ATMOSPHERE ON  
ADHERENCE OF VITREOUS COATINGS TO IRON

By A. G. Eubanks and D. G. Moore

National Bureau of Standards



Washington

May 1955

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## SUMMARY

A series of vitreous coatings of the same basic composition, but with cobalt-oxide contents varying from 0 to 6.4 percent by weight, was fired on ingot iron in atmospheres consisting of various oxygen-nitrogen mixtures. The effect of the oxygen content of the atmosphere on adherence was determined by subjecting each specimen to the American Society for Testing Materials adherence test, and the effect on interface roughness was estimated from examination of metallographic sections.

Results of the investigation showed that a decrease in the amount of oxygen in the firing atmosphere necessitated an increase in the amount of cobalt oxide in the enamel if optimum adherence was to be secured. It was also found that ground coats containing 3.2 weight percent or more of cobalt oxide developed a weak but definite bond in oxygen concentrations as low as 0.02 mole percent but that, when lower amounts of cobalt oxide were present in the enamel, a greater oxygen concentration in the furnace atmosphere was necessary for appreciable bond development.

When 2.0 percent of manganese dioxide was added to an enamel containing 0.4 weight percent cobalt oxide, the effect was small, but the trend was toward increased adherence.

Metallographic examinations of the interfaces of the various specimens tested showed a qualitative correlation between adherence and surface roughness regardless of the oxygen content of the firing atmosphere. This roughening of the iron surface was attributed to galvanic corrosion.

## INTRODUCTION

An earlier investigation conducted in the Enameled Metals Laboratory of the National Bureau of Standards has shown that a correlation exists between the roughness of the interface and the adherence of a porcelain-enamel ground coat to steel (ref. 1). A second study showed that a possible mechanism through which the roughness is generated is by galvanic

corrosion (ref. 2). The first reaction that occurs in the galvanic-corrosion mechanism as proposed by Dietzel (ref. 3) may be written as follows:  $\text{CoO (in the enamel)} + \text{Fe} \rightarrow \text{FeO} + \text{Co}$ . Another National Bureau of Standards study (ref. 4) confirmed that the cobalt shown on the right side of the equation plates out of the molten enamel electrolyte, presumably onto the more electronegative areas of the iron surface during the early stages of the firing operation. In view of this deposition, a minor amount of selective corrosion of the iron, with a corresponding slight bond development, should occur even when a specimen is fired in an atmosphere that is completely free of oxygen, although a more pronounced attack would be expected when the supply of oxygen is plentiful.

The earlier data on the relation between oxygen in the furnace atmosphere and bond development have all been qualitative. Cooke (ref. 5), in 1924, fired a cobalt-bearing commercial ground-coat enamel on iron in a nitrogen atmosphere and obtained very poor adherence. Other investigators (refs. 6, 7, and 8) have since substantiated Cooke's findings. Although all of the aforementioned investigations, including a more recent one at the National Bureau of Standards on the effect of the nickel dip (ref. 9), tend, in general, to give added support to the galvanic-corrosion theory, it was felt that quantitative data relative to the role played by oxygen in the development of adherence would help to indicate whether the theory should be accepted or rejected as a primary mechanism in the development of adherence between ground coats and iron.

The present work represents one further phase of a study on the general subject of ceramic-to-metal bonding that has been under way for some time at the National Bureau of Standards. This study is being carried forward under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

## MATERIALS

Ingot iron was used as the basis metal for all specimens. The metal blanks, 4 inches by 4 inches by 0.047 inch, were sheared to size, marked for identification, and punched to provide hanging holes. The blanks were prepared for coating by pickling and were neutralized after pickling in an aqueous solution of sodium cyanide and sodium hydroxide.

One basic frit composition and one mill-batch formula were used for preparing all of the coatings included in the study. The basic frit composition is given in table I and the mill batch, in table II. The cobalt-oxide contents of the frits were 0.0, 0.4, 3.2, and 6.4 percent by weight, expressed as a percentage of the basic frit composition, except that one frit had both 0.4 percent cobalt oxide and 2.0 percent manganese dioxide.

Each frit, with the appropriate metallic-oxide addition, was batched, smelted, and ball milled according to standard procedures.

All of the coatings were applied by dipping after being adjusted to give a dry thickness of 7 to 8 mils.

The gases used for preparing the furnace atmospheres were water-pumped oxygen and nitrogen of commercial purity. Analysis showed that the nitrogen contained 0.8 percent oxygen and that the oxygen had a purity of 99.1 mole percent, the balance being argon plus a trace of carbon dioxide. For a few of the tests the oxygen content of the nitrogen was reduced to 0.02 mole percent by passing the gas over copper turnings maintained at a temperature of 1,200° F. There was no other purification of the gases.

#### APPARATUS AND PROCEDURE

Figure 1 is a photograph of the apparatus used both for preparing the atmospheres and for firing the specimens; figure 2 is a schematic drawing of the same equipment.

In preparing for a test, the mixing chamber (container D in fig. 1) was first filled with water from a constant-head water supply. Then a previously selected volume of oxygen was permitted to flow into the chamber, the pressure in the oxygen tank being used to force the excess water out through the leveling-bottle (G in fig. 1) connection. The volume of oxygen was adjusted to atmospheric pressure by alining the water level in the leveling bottle with that in the mixing chamber. The desired amount of nitrogen was next introduced into the chamber using the same procedure as for oxygen. The mixture was then brought to atmospheric pressure using the method described above. The specimen to be fired was then suspended in the Inconel furnace muffle (A in fig. 1) and the muffle lid bolted into position. As shown in figure 2, a silicone rubber gasket was used between the lid and the upper part of the muffle to achieve a gas tight seal. Overheating of this gasket was prevented by a cooling coil placed beneath the upper flange of the muffle through which water was circulated. The muffle dimensions were approximately  $\frac{3}{4}$  inch by 5 inches by  $12\frac{1}{2}$  inches.

The system, which had a total volume of 1,800 milliliters, was evacuated to a pressure of 0.5 millimeter of mercury. The connection to the vacuum pump was then closed and the gas mixture permitted to flow slowly into the system until a positive pressure of 3.75 millimeters of mercury (2 inches of water) was achieved.

After a 2-minute flushing period, the flow through the muffle was adjusted to  $140 \pm 10$  milliliters per minute and a gas sample taken. Analyses of a number of these gas samples showed that in no case did the actual oxygen content vary more than 5 parts in 1,000 from that calculated. The atmospheres containing appreciable amounts of oxygen were analyzed chemically, while those containing small amounts of oxygen were analyzed with the mass spectrometer.

All gas mixtures were dried prior to entry into the furnace by passing them through towers filled with activated alumina (E in fig. 1). Several analyses for moisture content showed that the dew point of the gas after this drying treatment was  $-40^{\circ}$  F.

The induction coil surrounding the muffle was energized and the specimen heated according to a fixed schedule. The output from the 10-kilowatt radio-frequency generator (C in fig. 1) was so adjusted that the specimen reached the firing temperature of  $1,550^{\circ}$  F in  $2\frac{1}{4}$  minutes; it was subsequently held at this temperature for  $3\frac{3}{4}$  minutes to complete the firing.

The adherence of each specimen was evaluated by the Porcelain Enamel Institute adherence meter. This instrument, when used according to the A.S.T.M. test procedure (ref. 10), establishes the fraction of a test area, on a coated specimen that has been deformed in a prescribed manner, over which the coating continues to adhere in spite of the deformation.

The oxygen contents of the oxygen-nitrogen atmospheres used in firing the specimens were 0.02, 0.8, 5, 20, 40, 60, and 99.1 mole percent. The major impurities consisted of traces of argon and carbon dioxide.

Metallographic sections were prepared from the specimen in each group having the adherence value nearest the average for the group. These sections were examined to determine the degree of interface roughening. Photomicrographs were made of representative specimens.

## RESULTS AND DISCUSSION

Figure 3 shows the results obtained when the coatings of different cobalt content were fired in atmospheres containing various amounts of oxygen. As can be seen, the adherence index for the coating that contained no cobalt oxide was consistently zero, regardless of the oxygen

content of the atmosphere. If adherence were caused by the presence of a very thin layer of iron oxide at the interface, mutually soluble in the iron and in the ceramic, such as was first postulated by Kautz (ref. 8), it would seem logical to expect that a film of the proper thickness for good adherence would have formed between the coating that was free of cobalt and the iron at some oxygen content between 0.02 and 99.1 mole percent. The observation that no appreciable bonding develops with the cobalt-free coating suggests that the presence of such an oxide layer is not the key to adherence, at least in the case of vitreous enamel on iron.

While the presence of oxygen in any amount will not bring about adherence in an enamel that is free from the adherence-promoting oxides, it should not be overlooked that, even when these oxides are present, oxygen from some source is required for galvanic corrosion to occur (ref. 2).

The curve in Figure 3 for the coating with 0.4 percent by weight of cobalt oxide shows adherence values that are slightly lower, for the most part, than those for the same enamel with an addition of 2.0 percent of manganese dioxide. Manganese dioxide is recognized as an oxidizing agent and the effect observed when this material is present in a cobalt-bearing coating is probably related to its ability to furnish oxygen to the interface.

The coating containing 0.4 percent cobalt oxide developed its best adherence at an oxygen content of 20 mole percent, which approximates that of air, while the enamels with higher cobalt-oxide contents reached their peak adherences at about 5 mole percent of oxygen. This observation, that is, that enamels with larger amounts of adherence oxides do not require so much oxygen in the furnace atmosphere as those with lower amounts, indicates that oxygen can be supplied to the iron from the enamel itself. Since the only difference in the coatings is in the cobalt-oxide contents, it can be concluded that the cobalt oxide is in some way supplying or facilitating the supply of some of the necessary oxygen. This conclusion is substantiated by figure 4 which is a plot of the cobalt-oxide content versus adherence index for specimens fired in atmospheres having low concentrations of oxygen. These curves apparently intersect the origin, thus indicating that without cobalt the adherence index is zero. With increasing cobalt-oxide content, however, the adherence index increases accordingly. As shown in the curve for 0.02 mole percent oxygen, a weak but definite bond developed between the iron and the ground coat containing 3.2 percent cobalt oxide, and the strength of the bond was increased when 6.4 percent of cobalt oxide was added. On the other hand, coatings containing less than 3.2 percent cobalt oxide required a greater oxygen concentration in the firing atmosphere for equivalent adherence to develop, as evidenced by the curve for 5 mole percent oxygen. It is also apparent from figure 4 that lower oxygen contents of the atmosphere resulted in less effectiveness of the cobalt in improving adherence. It was impossible with the equipment used

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to achieve an atmosphere that was completely oxygen free, but the upward trend of the curves is such as to suggest that even in the absence of atmospheric oxygen some adherence would develop if the cobalt-oxide content of the coating were sufficiently high.

Figure 4 thus supplements figure 3 in showing that oxygen is required for bond development but that, in the absence of atmospheric oxygen, it can be supplied to the interface if cobalt oxide is present in the coating.

As mentioned in the introduction, a good correlation was shown to exist between the roughness of the enamel-iron interface and the adherence index in the case of specimens fired in an air atmosphere (ref. 1). To determine whether a similar correlation was indicated in the present investigation, numerous sections of coated specimens that had been fired in atmospheres of different oxygen-to-nitrogen ratios were examined with a metallographic microscope. Figure 5 shows a series of interfaces between iron and the coating that contained 0.4 percent of cobalt oxide, after firing in atmospheres containing increasing amounts of oxygen. In the case of the specimen fired in 0.8 mole percent oxygen, nickel plating was resorted to as a means of preserving the interface contour during the polishing operation, since the enamel came away from the iron while the cross section was being cut prior to mounting. Although the quantitative methods described in the earlier report (ref. 1) for evaluating surface roughness were not considered necessary for the present study, it is clear from observation alone that interface roughness increases with increasing oxygen content up to the point at which the oxygen content approximates that of air, that is, about 20 mole percent. At this point no further increase in the degree of roughness is apparent, nor is there any further increase in adherence. Similar behavior was also observed with enamels containing amounts of cobalt oxide other than 0.4 percent by weight, the roughness in each case increasing until a maximum adherence index was reached, after which both the roughness and adherence index remained substantially constant.

A correlation between surface roughness and adherence index is apparent also in figure 6. These micrographs, which are of coated specimens fired in an atmosphere containing only 0.02 mole percent oxygen, show an increasing roughening with increasing cobalt-oxide content. Here, again, nickel plating was resorted to as a means of preserving the interface of the specimen of enamel containing 0.4 percent cobalt oxide.

The data obtained clearly show, therefore, that a qualitative correlation exists between surface roughness and adherence, and they further show that the generation of surface roughness is dependent not only on the availability of oxygen at the interface but also on the presence of an adherence-promoting oxide, such as cobalt oxide, in the coating layer. These data also show that, when there is a lack of oxygen in the furnace

atmosphere, a significant development of surface roughness and adherence will still occur if sufficient cobalt oxide is present to cause an oxidizing condition at the interface. Manganese oxide, in the presence of cobalt oxide, also appears to promote adherence to a limited extent.

The galvanic-corrosion theory requires that only very small amounts of cobalt oxide are needed in the coating to form galvanic cells. Once these cells are formed, selective etching of the iron surface will occur if the specimen is fired in an atmosphere containing a sufficient amount of oxygen. In an oxygen-deficient atmosphere, on the other hand, little or no selective etching will occur because there is insufficient oxygen present to promote the corrosion of the exposed areas of iron. However, the oxygen required for the corrosion process does not need to come necessarily from the furnace atmosphere. If easily reducible oxides are present in the coating layer, then selective corrosion of the iron can still occur even in a furnace atmosphere that is substantially free of oxygen.

Thus, the data obtained can be readily explained on the basis of the galvanic-corrosion theory. The importance of this mechanism in accounting for the adherence of vitreous enamels to steel has experimental confirmation in the correlation that has been shown to exist between interface roughness and adherence index, both in the present investigation and in earlier studies (refs. 1 and 9). There is also evidence (ref. 2), however, that roughness of interface does not completely account for adherence. Specifically, poor adherence has been observed on very rough interfaces having high anchor-point counts. Also, in the case of coatings on alloys, fairly good adherence has been obtained without surface roughening. Thus, although the observations made in the present investigation can be explained on the basis of the galvanic-corrosion theory, it is the authors' opinion that bond development is not wholly dependent on mechanical anchoring but that some other factors are active. Future work should be directed toward the isolation of these other active mechanisms.

National Bureau of Standards,  
Washington, D. C., July 15, 1954.



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TABLE I

BASIC COMPOSITION OF FRIT USED FOR PREPARING VARIOUS GROUND COATS

## (a) Batch composition

Material	Parts by weight
Potash feldspar	30.82
Borax (hydrated)	44.25
Flint	30.50
Soda ash	9.16
Soda niter	5.15
Fluorspar	8.30
	<u>128.18</u>

## (b) Computed oxide composition

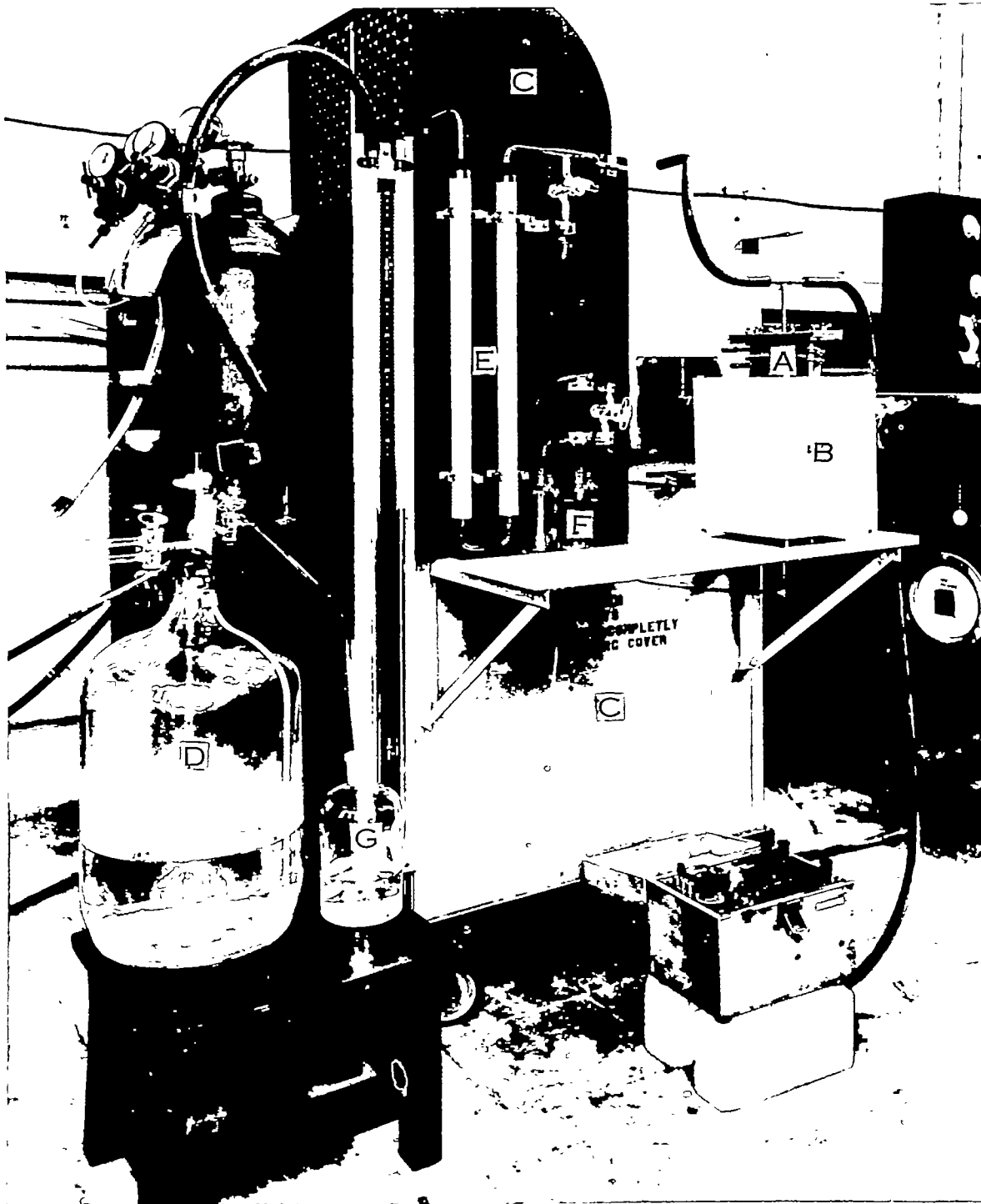
Oxide	Percent by weight
$\text{SiO}_2$	51.0
$\text{B}_2\text{O}_3$	16.1
$\text{Al}_2\text{O}_3$	5.7
$\text{Na}_2\text{O}$	15.4
$\text{K}_2\text{O}$	3.5
$\text{CaF}_2$	8.3
	<u>100.0</u>

TABLE II

## MILL BATCH USED FOR PREPARING GROUND-COAT SLIPS

[Milling time, 3 hr; fineness, 10g on 200 mesh  
from 50 ml of slip]

Material	Weight, g
Frit	1,000
Enameler's clay	60
Borax	10
Water	425



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Figure 1.- Photograph of atmosphere-mixing and firing apparatus. A, firing muffle; B, insulating shell; C, induction heating unit; D, glass mixing container; E, drying towers; F, bubbling bottle at exhaust outlet; and G, leveling bottle.

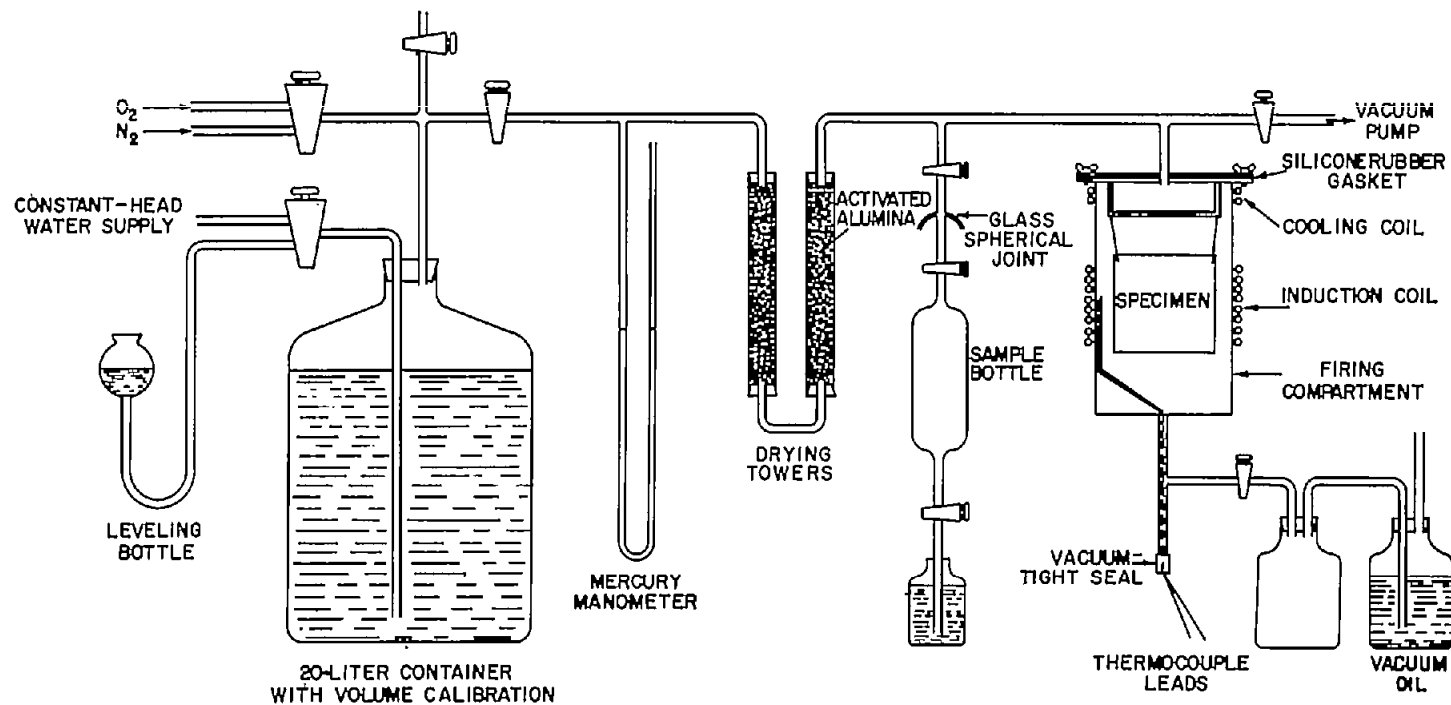


Figure 2.- Schematic drawing of atmosphere-mixing and firing apparatus shown by photograph in figure 1.

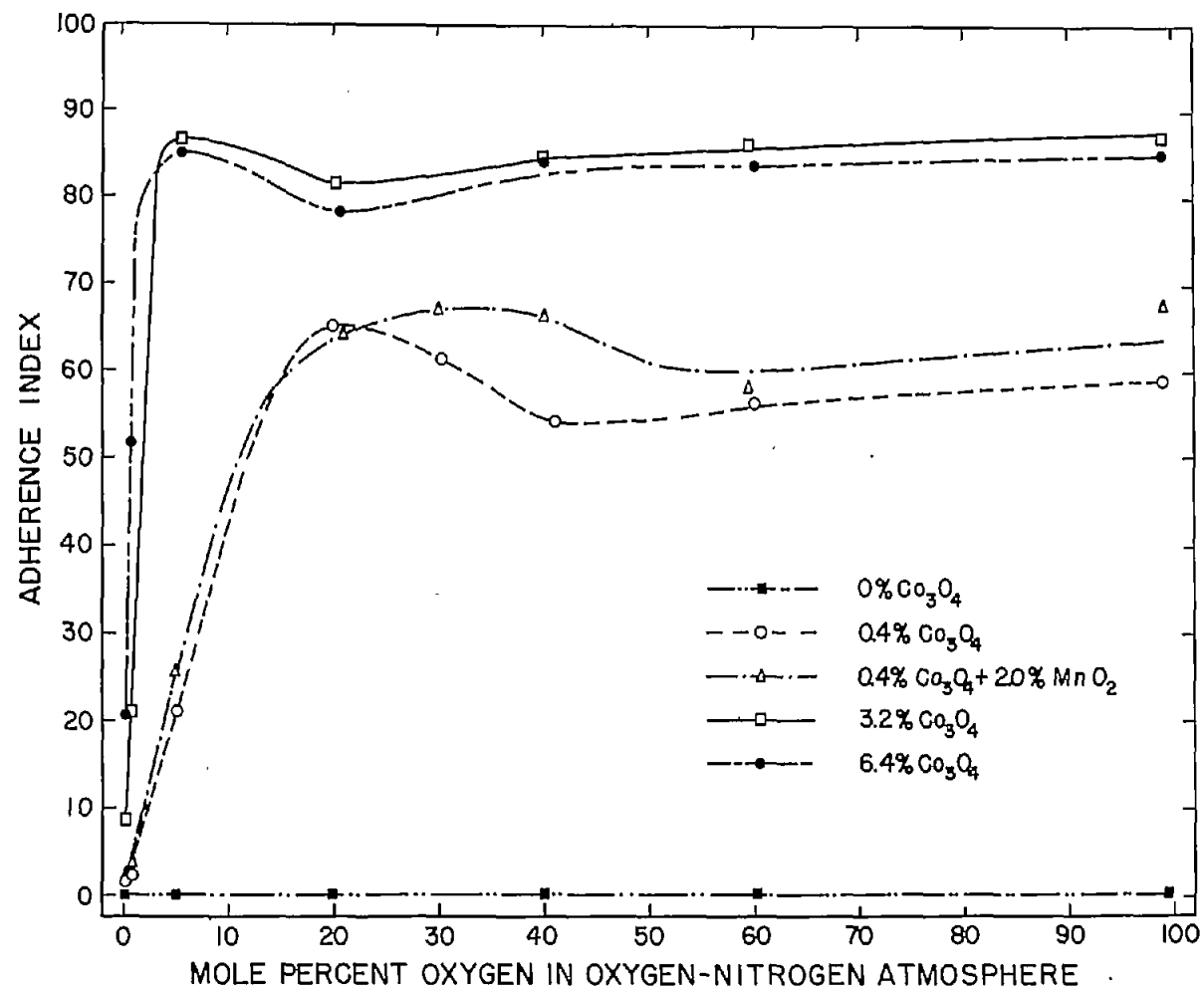


Figure 3.- Plot of adherence index versus oxygen content of firing atmosphere showing effect of oxygen on adherence developed between ingot iron and a vitreous coating containing various metallic-oxide additions.

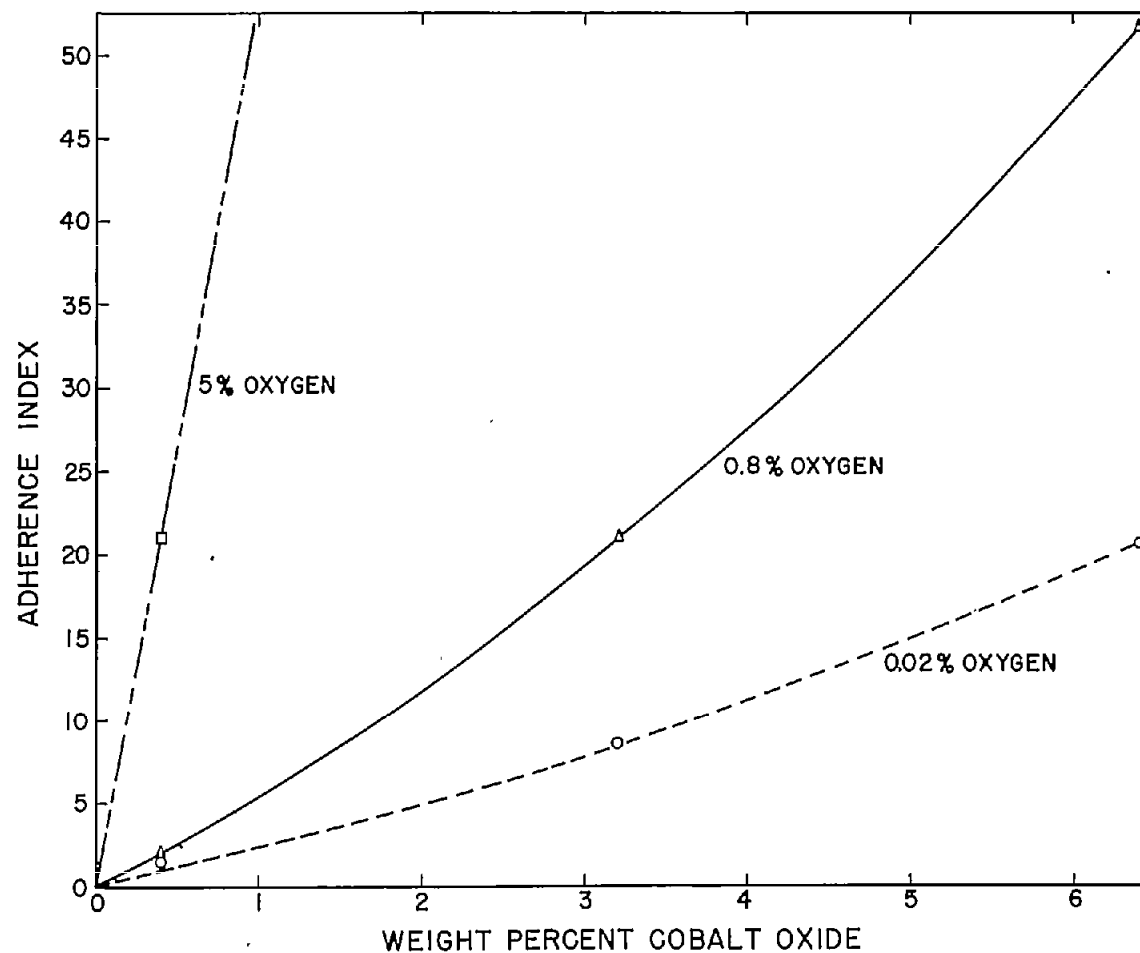
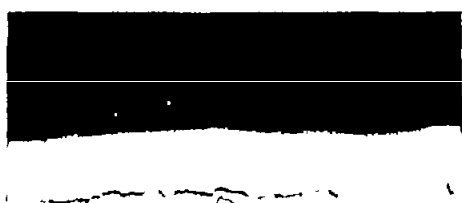


Figure 4.- Effect of cobalt oxide in enamel on adherence developed when coating was fired on iron in nitrogen atmospheres of low oxygen concentration. Only one point is given on the curve for 5 percent oxygen, but data that could not be plotted on the scale selected indicate that this curve, like the others, passes through the origin. Oxygen concentrations are in mole percent.





(a) 0.8 percent oxygen;  
adherence index, 2.1.



(b) 5.2 percent oxygen;  
adherence index, 21.0.



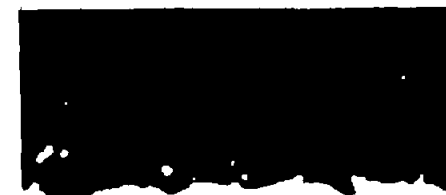
(c) 20.0 percent oxygen;  
adherence index, 65.0.



(d) 41.2 percent oxygen;  
adherence index, 54.2.



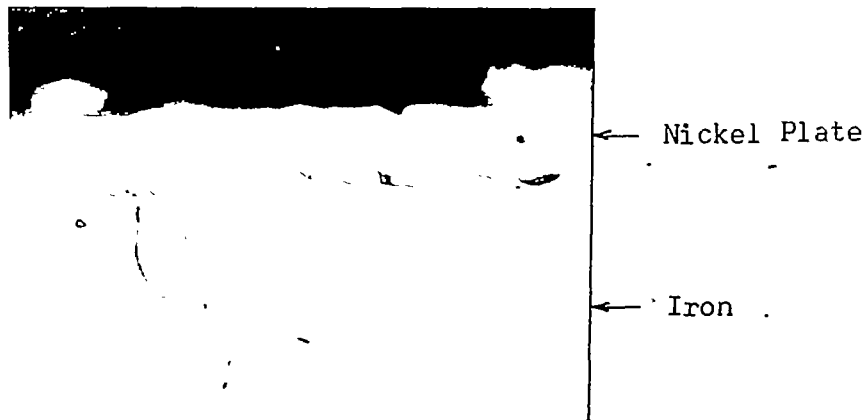
(e) 60.0 percent oxygen;  
adherence index, 56.2.



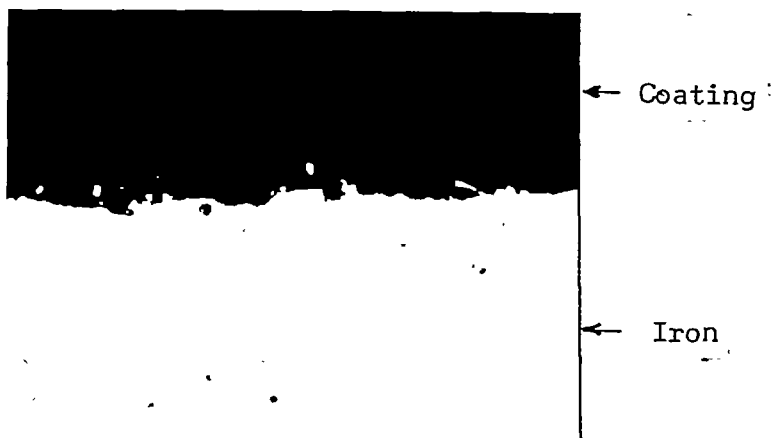
(f) 99.1 percent oxygen;  
adherence index, 58.6.

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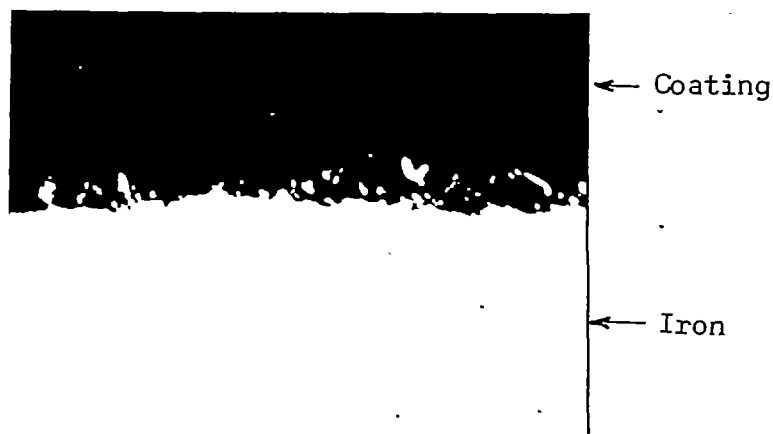
Figure 5.- Micrographs of coated iron specimens showing effect of oxygen content of furnace atmosphere on surface roughness for a coating containing 0.4 percent cobalt oxide by weight. Coating on specimen fired in atmosphere with 0.8 mole percent oxygen flaked from metal during cutting operations, and the section was subsequently nickel plated to preserve the interface. X900, unetched.



(a) 0.4 percent cobalt oxide; adherence index, 1.5.



(b) 3.2 percent cobalt oxide; adherence index, 8.6.



(c) 6.4 percent cobalt oxide; adherence index, 20.6.

Figure 6.- Micrographs of coated iron specimens fired in a nitrogen atmosphere that contained only 0.02 mole percent oxygen. Nickel plating was applied in (a) to preserve the interface inasmuch as coating had flaked off while section was being cut. X900, unetched.